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(57) Abstract

A process for preparing a nanocrystalline material comprising at least a first ion and at least a second ion different from the first ion, and wherein at least the first ion is a metal ion, is described. The process comprises contacting a metal complex comprising the first ion and the second ion with a dispersing medium suitable to form the nanocrystalline material and wherein the dispersing medium is at a temperature to allow formation by pyrolysis of the nanocrystalline material when contacted with the metal complex.

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PROCESS FOR PREPARING A NANOCRYSTALLINE MATERIAL

The present invention relates to a process. In particular, the present invention relates to a process for synthesising nanocrystalline materials, such as nanocrystalline CdSe.

Nanocrystalline materials, which are sometimes referred to as nanoparticles, Q-particles, quantum dots or nanocrystallites, have been recognised as suitable systems for studying the transition from the molecular to the macrocrystalline level and have been extensively studied in the recent years.[1-11]

Interest in research into new synthetic routes for semiconductor nanocrystallites is now enhanced as devices based on such materials have been fabricated.[12-14] A number of synthetic methods have been reported for the preparation of a wide range of semiconductor nanoparticles[1-7, 15-23].

Known processes for preparing nanocrystalline materials, such as nanocrystalline CdSe, have included arrested precipitation in micelles[21] or the reaction of molecular species at high temperature in organic solvents.[22-25].

In more detail, Murray *et al*[22] report on the preparation of CdE (where E is S, Se or Te) by the pyrolysis of two organometallic reagents by injection into a hot coordinating solvent. In particular, the Murray process involves injecting a solution of $(CH_3)_2Cd$ in TOP (tri-*n*-octylphosphine) into a hot solution of TOP containing Se (TOPSe and TOP). Alternatively, any one of $(TMS)_2S$ (bis(trimethylsilyl)sulphide), $(TMS)_2Se$ (bis(trimethylsilyl)selenide), and $(BDMS)_2Te$ (bis(*tert*-butyldimethylsilyl)tellurium) may be used instead of TOPSe.

In the Murray process $(CH_3)_2Cd$ is chosen as the only Cd source. Moreover, Murray *et al* state that $(TMS)_2Se$ or TOPSe and TOPTe are selected as chalcogen sources with TOPSe and TOPTe preferred due to their ease of preparation and their stability.

Chemical reactions in TOPO (tri-*n*-octylphosphine oxide) are also described by Murray[24]. These processes have been used to prepare nanocrystallites of II/VI semiconductors[12,13,24,25]. In this instance, TOPO is used as dispersing medium and a metal source (e.g $Cd(CH_3)_2$) and a chalcogenide source (e.g. TOPSe) are injected into the hot TOPO (typically at 250°C) to form CdSe nanocrystallites. The size distribution of the semiconductor can be controlled by the temperature of heating during the synthesis and by size selective precipitation of the final material.[24,25]

A refinement of the Murray process has been proposed by Katari *et al*[23]. As with the Murray process, in the Katari process CdE is prepared by the pyrolysis of two organometallic reagents by injection into a hot coordinating solvent. In the Katari process Se is dissolved in TBP (tributylphosphine) to which $(CH_3)_2Cd$ is then added. The resultant $(CH_3)_2Cd/Se$ solution is then added to a heated solution of TOPO.

As with the Murray process, in the Katari process $(CH_3)_2Cd$ is chosen as the only Cd source.

There are however problems associated with the prior art processes for preparing nanocrystalline materials. For example, both the Murray process (*ibid*) and the Katari process (*ibid*) involve the use of hazardous chemicals, in particular $(CH_3)_2Cd$. In this regard, $(CH_3)_2Cd$ is toxic, volatile and extremely difficult to handle. Moreover, on exposure to air it undergoes spontaneous combustion.

Aside from using the hazardous compound $Cd(CH_3)_2$ [12,13] to prepare nanocrystalline CdSe, other workers have used the equally hazardous H_2Se[14] for the synthesis of the CdSe.

The present invention seeks to overcome the problems associated with the prior art processes for making nanocrystalline materials.

According to a first aspect of the present invention there is provided a process for preparing a nanocrystalline material comprising at least a first ion and at least a second ion different from the first ion, and wherein at least the first ion is a metal ion, the process comprising contacting a metal complex comprising the first ion and the second ion with a dispersing medium suitable to form the nanocrystalline material and wherein the dispersing medium is at a temperature which allows formation of the nanocrystalline material by pyrolysis when contacted with the metal complex.

According to a second aspect of the present invention there is provided a nanocrystalline material obtained by the process of the present invention.

According to a third aspect of the present invention there is provided a device comprising a nanocrystalline material obtained by the process of the present invention.

Preferably the metal ion is a divalent metal ion or a trivalent metal ion.

Preferably the metal ion is selected from a cadmium ion, a zinc ion, a lead ion, a mercury ion, an indium ion and a gallium ion, including combinations thereof.

Preferably the second ion is selected from an oxide ion, a selenide ion, a sulphide group, a phosphide group or an arsenide ion, or combinations thereof.

Preferably the second ion is or is part of a thiol-carbamate group or a seleno-carbamate group.

Preferably the second ion is or is part of a dithiol-carbamate group or a diseleno-carbamate group.

Preferably the metal complex additionally comprises an organic group and/or thio group. The organic group can be an alkyl group or an aryl group, which may be substituted.

Preferably the organic group is an alkyl group, which may be substituted and/or unsaturated.

Preferably the organic group is a dialkyl group, which may be substituted and/or unsaturated, and/or wherein the thio group is a dithio group.

Preferably the organic group is a di-C_{1-6}alkyl group and/or the thio group is a dithio group or a diseleno group.

Preferably the organic group is a diethyl group.

Preferably the dispersing medium is at a temperature of 250°C or more, preferably about from 300°C to 350°C.

Preferably the dispersing medium passivates the surface of the nanocrystalline material.

Preferably the dispersing medium is TOPO, or a related coordinating medium, including combinations thereof. Another dispesing medium could be TBP.

Preferably the nanocrystalline material comprises or is selected from any one of cadmium selenide, cadmium sulphide, zinc selenide, zinc sulphide, indium phosphide and gallium arsenide, including ternary and quaternary combinations thereof.

Preferably the nanocrystalline material is cadmium selenide.

Preferably the metal complex is diethyl diselenocarbamato cadmium or dithio diselenocarbamato cadmium, or related mixed alkyl complexes thereof.

Preferably the device is an optical device.

Preferably the device is any one of a non-linear optic device, a solar cell or an LED.

Preferably the device is an LED.

Preferably the device is a blue LED.

The present invention is therefore based on the surprising finding that nanocrystalline materials can be prepared by using as a reactant a metal complex which provides at least two of the ions of the nanocrystalline material. The process of the present invention is therefore very different to the Murray process (*ibid*) and the Katari process (*ibid*) wherein in each of those processes it is necessary to use two independent sources to provide at least two of the ions of the nanocrystalline material. Thus, the use of a molecular precursor containing both elements in the present process provides an attractive route to metal selenides, especially if a large scale preparation is anticipated.

The present invention is further advantageous over the prior art processes as it does not rely on the use of hazardous chemicals such as $(CH_3)_2Cd$.

The present invention is further advantageous as it provides a low cost route to prepare photovoltaic materials and optoelectronic materials, preferable examples of which include non-linear optic devices, solar cells and LEDs.

Thus the present invention shows that a single source can be used in a dispersing medium, such as TOPO, to replace the use of the hazardous metal alkyls. In a highly preferred embodiment, the present invention provides the synthesis of CdSe nanocrystallites using methyl diethyldiselenocarbamato cadmium (II) MeCddsc: $[(CH_3)CdSe_2CN(C_2H_5)_2]_2)$ as a precursor. The synthetic method of this preferred embodiment is diagrammatically illustrated in Figure 1, which makes no efforts to represent a mechanistic pathway.

Even though the pathway shown in Figure 1 is for the synthesis of CdSe it is to be understood that the process of the present invention is useful for preparing a series of

nanocrystalline materials.

Examples of nanocrystalline materials that can be prepared using an appropriate single molecule precursor can be represented by the general formulae A and B as shown below.

$M^{II}E$ GENERAL FORMULA A

wherein M is Zn, Cd, Hg or a divalent transition metal; and wherein E is O, S, Se, P, or As.

$M^{III}{}_xE_y$ GENERAL FORMULA B

wherein M is Al, In, Ga or a trivalent transition metal; and wherein E is O, S, Se, P, or As; and wherein x and y are appropriate intergers.

Formulae A and B also encompass related ternary systems.

Therefore, examples of nanocrystalline materials other than cadmium selenide include cadmium sulphide, zinc selenide, zinc sulphide, indium phosphide and gallium arsenide.

The general formula of the metal complex for use in the process of the present invention can be represented as:

ML_n FORMULA I

wherein M represents a metal ion; L represents one or more ligands which need not be the same; n represents the valency of the metal; and wherein M is the first ion of the nanocrystalline material and at least one L provides the second ion for the nanocrystalline material.

Typically M is a divalent metal ion or a trivalent metal ion, such as any one of cadmium, zinc, lead, mercury, indium gallium, including combinations thereof.

Typically L is any one of an oxide ion, a selenide ion, a sulphide group, a phosphide group or an arsenide ion, or combinations thereof. More in particular L is or is part of any one of a thiol-carbamate group or a seleno-carbamate group, such as a dithiol-carbamate group or a diseleno-carbamate group.

In a preferred embodiment, at least one L is an organic group and/or a thio group. If at least one L is an organic group then preferably that organic is an alkyl group, which may be substituted and/or unsaturated, such as a C_{1-10} (preferably C_{1-6}, more preferably C_{1-4}) alkyl group, which may be substituted and/or unsaturated.

Preferably, at least one L is a dialkyl group, which may be substituted and/or unsaturated, and/or wherein the thio group is a dithio group. Preferably, the organic group is a di-C_{1-6} alkyl group and/or the thio group is a dithio group or a diseleno group. In a highly preferred embodiment, at least one L is a diethyl group.

Typical general formulae for suitable metal complexes containing at least one organic group for use as single molecule precursors in the process of the present invention are shown below as Formula II (for metals that are divalent) and as Formula III (for metals that are trivalent):

$$[R^{II} - M^{II} - (E_xCNRR^I)_y]_z \qquad \text{FORMULA II}$$

$$[(R^{II})(R^{III}) - M^{III} - (E_xCNRR^I)_y]_z \qquad \text{FORMULA III}$$

wherein R, R^I, R^{II} and R^{III} independently represent an aryl or alkyl group as defined above, which may be substituted and/or unsaturated; M^{II} is a divalent metal ion; M^{III} is a trivalent metal ion; E is any one of an oxide ion, a selenide ion, a sulphide group,

a phosphide group or an arsenide ion, or combinations thereof (such as, by way of example, -O-S-); x is an integer, preferably 2; y is an integer; and z is an integer, usually 1 or 2.

As mentioned above, a highly preferred metal complex containing at least one organic group for use as a single molecule precursor in the process of the present invention is methyl diethyldiselenocarbamato cadmium (II) (MeCddsc) wherein R is C_2H_5; R^I is C_2H_5; R^{II} is (CH_3); M is Cd^{II}; E is Se; x is 2; y is 1; and z is 2.

However, other preferred metal complexes containing at least one organic group for use as single molecule precursors in the process of the present invention include

$$M - (E_2CNAlk_2)_n \qquad \text{FORMULA IV}$$

wherein n is 2 for metals such as zinc, cadmium and lead; n is 3 for metals such as gallium or indium; E is S or Se; and A is an aryl or alkyl group, preferably ethyl; including carbamate (i.e. O-donors) thereof:

and either

$$R^{II} - M - (E_2CNA_2)_n \qquad \text{FORMULA V}$$

or

$$(R^{II})_n - M - (E_2CNA_2) \qquad \text{FORMULA VI}$$

wherein n is 1 for metals such as zinc, cadmium and lead; n is 2 for metals such as gallium or indium; E is S or Se; A is an aryl or an alkyl group, preferably ethyl; and R^{II} is independently selected from an alkyl or aryl group as defined above, such as methyl.

Other possible metal complexes for use as single molecule precursors in the process of the present invention include related thiolates, thiophosphinates or phosphinochalcogens and related selenium containing compounds.

The present invention will now be described only by way of examples. In the examples, reference is made to the attached Figures wherein

Figure 1 is a scheme of the synthetic method of CdSe nanocrystallites using a single source;

Figure 2 is an optical absorption spectrum of CdSe nanocrystallites dispersed in toluene (fraction 3) - the inset shows the particle size distribution of the same sample as determined by TEM; and

Figure 3 is a fluorescence emission spectra of size fractionated CdSe (λexc = 465 nm).

Experimental

1. <u>Preparation of nanocrystalline cadmium selenide</u>

1.1 MeCddsc was synthesised by the comproportionation reaction[27] between $Cd(CH_3)_2$ (Epichem) and bisdiethyldiselenocarbamato cadmium (II) in dry toluene, at room temperature, using Schlenk techniques and a nitrogen atmosphere. The TOPO (90 %, Aldrich) was purified using the method described in the literature.[28] The identity of MeCddsc and the purity of TOPO were checked by ^1H nmr and IR spectroscopy and melting point measurements.

1.2 MeCddsc (0.5 mmol) was placed in 10 ml of TOP (98 %, Aldrich) and the mixture formed was filtered after which was injected in 30 g of TOPO at 200°C. The temperature of the solution was then raised to 250°C and heated for half an hour. The deep red solution that formed was allowed to cool down to 75°C after which a large

excess of dry CH_3OH (BDH) was added. A flocculate precipitate formed and was isolated by centrifugation and redispersed in toluene, any insoluble material was then discarded. The toluene was pumped off under vacuum (10^{-2} Torr) to give a deep red material which was washed with CH_3OH. The solid was redispersed in toluene to give solutions with a Port wine red colour which remained optically clear for weeks. Size selective precipitation was performed by adding CH_3OH to this solution until turbidity was observed followed by centrifugation the solid. This procedure was successively applied to the supernatant solutions obtained during the fractionation process until no optical absorption was detected.

1.3 The toluene solutions containing the nanocrystallites were characterised by optical absorption spectroscopy (Philips PU 8710 spectrophotometer) and fluorescence emission spectroscopy (Perkin Elmer LS50 luminescence spectrometer), at room temperature. The fluorescence spectra were normalized with the maximum set to one hundred. The X-ray powder diffraction experiments were performed using a Philips 1130 X-ray generator and a Guinier camera. Conventional transmission electron microscopy (TEM) of the nanocrystallites was performed using a JEOL-JEM 1200 EX II scanning and transmission electron microscope, operating at 100 kV, on samples deposited over carbon coated copper grids. The histogram was obtained after measuring the diameter of around 300 nanoparticles shown on the TEM images. High resolution transmission electron microscopy (HRTEM) was performed using a JEOL FX 2000 instrument, operating at 200 kV, on samples deposited over carbon coated copper grids.

1.4 The optical absorption spectrum of a toluene solution containing nanodispersed CdSe obtained from the thermal decomposition of MeCddsc is shown in Figure 2. The absorption edge of the spectrum is clearly blue shifted in relation to the bulk band gap of CdSe (716 nm, 1.73 eV) suggesting the presence of nanoparticles with sizes below the bulk exciton dimensions of CdSe. The maximum observed in the optical spectrum of nanodispersed CdSe has been associated with the lowest energy electronic transition occurring in the CdSe nanocrystallites.[21-25]

1.5 The emission fluorescence spectra of different size fractionated samples of CdSe are depicted in Figure 3. The size selective precipitation is based on the fact that the largest particles are the first to precipitate, due to the stronger Van der Waals interactions, on the addition of a non-solvent to the nanodispersed material. Using this procedure it is possible to obtain initial solid fractions richer in larger particles as compared with the later fractions. The maximum of the emission band in Figure 3 is gradually blue shifted as the size distributions become weighted of smaller dimensions particles. Such shifts on the band edge (Figure 2) and band maximum (Figure 3) in the absorption and emission spectra, respectively, have been reported as an evidence of quantum size effects.[1-7]

1.6 The fluorescence spectrum of fraction 3 corresponds to the optical absorption spectrum in Figure 2. The emission band maximum is observed at a wavelength close to the absorption edge of the optical spectrum (band edge emission); the typical red emission due to the recombination of charge carriers on deep traps located at the particles surface was not detected. These results suggest that surface coverage with TOPO molecules should have occurred on the CdSe nanocrystallites.[2,24-26] The energy dispersive analysis X-ray results (EDAX) for CdSe nanocrystallites (after several washings with methanol) still show the presence of phosphorous, suggesting that the TOPO molecules are quite firmly bond to the CdSe nanocrystallites.

1.7 The dark red powder obtained from the synthesis gave an X-ray diffraction pattern consistent with hexagonal CdSe. The TEM image of the fraction 3 of CdSe giving the spectra in Figure 2 and Figure 3 was studied. The mean particle diameter of the nanocrytalline material was found to be 51.9 $\pm$ 7.4 Angstroms. The TEM results show that the CdSe nanocrystallites are approximately spherical and close to monodispersed. On the basis of the effective mass approximation[4] the excitonic peak located at 568 nm (2.18 eV) suggests the presence of CdSe nanoparticles with a diameter close to 57 Angstroms, discrepancies between the experimentally measured particle diameter and the predictions of the effective mass approximation have been reported by other authors.[24]

1.8 The crystallinity of the CdSe nanoparticles was confirmed by HRTEM. The HRTEM images showed the typical hexagonal pattern of the wurtzite structure for some of the particles in agreement with the X-ray powder diffraction results. The analysis of several images are consistent with the presence of some CdSe nanocrystallites with stacking faults. This type of defect for CdSe nanocrystallites has been reported by other authors[24]. Alivisatos *et al.* [25] reported the synthesis of CdSe nanocrystallites, using a TOPO method at higher temperatures for which no stacking faults were detected.

2. Preparation of nanocrystalline indium sulphide

2.1 Initially $Me_2InS_2CNEt_2$ was prepared by a comproportionation reaction between stoichiometric amounts of tris(diethyldithiocarbarmato)indium(III) (5.7g, 10.2 mmol) and trimethylindium (3.3 g) in toluene (40 mL). The mixture was stirred at room temperature for half an hour and then heated to 50°C and stirred for further 10 min. On concentration, white crystals settled out from the clear solution (7.90 g, 88%), mp 84°C.

2.2 The compound prepared by the process of 2.1 was then used to replace MeCddsc in Section 1.2 (*supra*). The product, nanocrystalline indium sulphide, was then analysed using the methods outlined in Sections 1.4 - 1.8 (*supra*).

3. Preparation of nanocrystalline gallium sulphide

3.1 Initially $Me_2GaS_2CNEt_2$ was prepared by a comproportionation reaction between stoichiometric amounts of tris(diethyldithiocarbarmato)gallium(III) and trimethylgallium in toluene (40 mL). The mixture was stirred at room temperature for half an hour and then heated to 50°C and stirred for further 10 min. On concentration, crystals settled out from the solution.

3.2 The compound prepared by the process of 3.1 was then used to replace MeCddsc in Section 1.2 (*supra*). The product, nanocrystalline gallium sulphide, was

then analysed using the methods outlined in Sections 1.4 - 1.8 (*supra*).

4. Preparation of other precursors for the preparation of nanocrystalline indium sulphide and nanocrystalline gallium sulphide

4.1 The precursor molecules described in Sections 2.1 and 3.1 could be respectively replaced with $Et_2InS_2CNEt_2$, $Np_2InS_2CNEt_2$, $Et_2GaS_2CNEt_2$, and $Np_2GaS_2CNEt_2$. In this regard these compounds were prepared by the following general protocol, which refers to the preparation of $Et_2InS_2CNEt_2$ though of course the other compounds are prepared by use of similar and appropriate reactants.

4.2 $Et_2InS_2CNEt_2$ was prepared by adding sodium diethyldithiocarbarmate (2.73 g, 15.97 mmol) to a solution of chlorodiethylindium (3.33 g, 15.97 mmol) in ether (60 mL) and stirred for 12 h at room temperature. A white solid (NaCl) formed during the reaction which was removed by filtration. The colourless filtrate containing the product was evaporated to dryness under vacuum. The solid product contained traces of salt and was dissolved in petroleum spirits (60-80°C) and filtered. The filtrate, on concentration, gave white crystals of diethyldiethyldithiocarbamatoindium (III) (3.33 g, 65%), mp 57°C.

4.3 As mentioned above, $Np_2InS_2CNEt_2$ was prepared in a similar manner and was obtained as a white crystalline solid (2.97 g, 70%), mp 44 °C.

4.4 As mentioned above, $Et_2GaS_2CNEt_2$ (4.51 g, 75%) and $Np_2GaS_2CNEt_2$ (3.25 g, 72%), both liquids, were prepared in a similar manner.

4.5 The compounds of 4.1 to 4.4 were then used to replace MeCddsc in Section 1.2 (*supra*). The respective nanocrystalline products were then analysed using the methods outlined in Sections 1.4 - 1.8 (*supra*).

5. Preparation of nanocrystalline zinc sulphide

5.1 Initially $[Zn[S_2CNMe^iPr]_2]_2$ was prepared as follows. A mixture of "zinc hydroxide" (4.77 g, 48 mmol), N-methylisopropylamine (10 ml, 96 mmol) and carbon disulphide (5.76 ml, 96 mmol) were suspended in ethanol and stirred at ca. 60°C for 2 hours. On cooling, the reaction mixture was filtered affording a white solid which was then dried at room temperature *in vacuo* and recrystallised from acetone. Yield 11.7 g, 67.6%.

5.2 The compound prepared by the process of 5.1 was then used to replace MeCddsc in Section 1.2 (*supra*). The product, nanocrystalline zinc sulphide, was then analysed using the methods outlined in Sections 1.4 - 1.8 (*supra*).

6. Preparation of nanocrystalline cadmium sulphide

6.1 Initially $[Cd[S_2CNMe^iPr]_2]_2$ was prepared as follows. A mixture of cadmium hydroxide, N-methylisopropylamine and carbon disulphide were suspended in ethanol and stirred at ca. 60°C for 2 hours. On cooling, the reaction mixture was filtered affording a solid which was then dried at room temperature *in vacuo* and recrystallised from acetone.

6.2 The compound prepared by the process of 6.1 was then used to replace MeCddsc in Section 1.2 (*supra*). The product, nanocrystalline cadmium sulphide, was then analysed using the methods outlined in Sections 1.4 - 1.8 (*supra*).

7. Preparation of nanocrystalline zinc arsenide

7.1 Initially $[Zn[As_2CNMe^iPr]_2]_2$ was prepared by appropriately adapting the process of Section 5.1 (*supra*).

7.2 The compound prepared by the process of 7.1 was then used to replace MeCddsc in Section 1.2 (*supra*). The product, nanocrystalline zinc arsenide was then analysed using the methods outlined in Sections 1.4 - 1.8 (*supra*).

8. Preparation of nanocrystalline cadmium arsenide

8.1 Initially $[Cd[As_2CNMe^iPr]_2]_2$ was prepared by appropriately adapting the process of Section 6.1 (*supra*).

8.2 The compound prepared by the process of 8.1 was then used to replace MeCddsc in Section 1.2 (*supra*). The product, nanocrystalline cadmium arsenide was then analysed using the methods outlined in Sections 1.4 - 1.8 (*supra*).

9. Preparation of further nanocrystalline materials

9.1 The following compounds were used to replace MeCddsc in Section 1.2 (*supra*). The respective nanocrystalline materials were then analysed using the methods outlined in Sections 1.4 - 1.8 (*supra*).

9.2 The following commentary describes the preparation of $(C_5H_{11})_2GaP^tBu_2$, however the process can be appropriately adapted for the preparation of $(C_5H_{11})_2IndiumP^tBu_2$, $(C_5H_{11})_2GalliumAsBu_2$, and $(C_5H_{11})_2IndiumAsBu_2$.

9.3 To prepare $(C_5H_{11})_2GaP^tBu_2$, LiP^tBu_2 was initially prepared by the addition of HP^tBu_2(5 g, 33.4 mmol) to a stirred solution of ^nBuLi (14.24 cm^3 of 2.5 M solution in hexanes, 35.6 mmol) diluted further with petroleum spirits (60-80°C, 50 cm^3, 0°C). The solution was left to stir overnight, concentrated, and then left to crystallise. $(C_5H_{11})_2GaCl(2)$ (2.56 g, 10.34 mmol) was dissolved in ether (60 cm^3) and stirred at 0°C. LiP^tBu_2 (1.57 g, 10.33 mmol) was slowly added and the mixture was allowed to reach ambient temperature. After stirring overnight, the solvent was removed under vacuum leaving a white solid. Petroleum spirits (60-80°C) (30 cm^3) were added to the solid. After decanting the supernatant, the solution was concentrated and left to crystallise at -25°C. Colourless, triangular shaped crystals formed, yield 3.12g, (84 %), m.p. 81°C.

10. Summary

The results reported here clearly show that nanocrystalline materials such as nanocrystalline MeSe can be easily prepared from molecular compounds such as MeCddsc. Moreover, these prepared nanocrystalline materials can be used as or in high quality semiconductors.

Other modifications of the present invention will be apparent to those skilled in the art.

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CLAIMS

1. A process for preparing a nanocrystalline material comprising at least a first ion and at least a second ion different from the first ion, and wherein at least the first ion is a metal ion, the process comprising contacting a metal complex comprising the first ion and the second ion with a dispersing medium suitable to form the nanocrystalline material and wherein the dispersing medium is at a temperature to allow formation by pyrolysis of the nanocrystalline material when contacted with the metal complex.

2. A process according to claim 1 wherein the metal ion is a divalent metal ion or a trivalent metal ion.

3. A process according to claim 1 or claim 2, wherein the metal ion is selected from a cadmium ion, a zinc ion, a lead ion, a mercury ion, an indium ion and a gallium ion, including combinations thereof.

4. A process according to any one of the preceding claims wherein the second ion is selected from an oxide ion, a selenide ion, a sulphide group, a phosphide group or an arsenide ion, or combinations thereof.

5. A process according to any one of the preceding claims, wherein the second ion is or is part of a thiol-carbamate group or a seleno-carbamate group.

6. A process according to claim 5, wherein the second ion is or is part of a dithiol-carbamate group or a diseleno-carbamate group.

7. A process according to any one of the preceding claims, wherein the metal complex additionally comprises an organic group and/or a thio group.

8. A process according to claim 7, wherein the organic group is an alkyl group, which may be substituted and/or unsaturated.

9. A process according to claim 7 or claim 8, wherein the organic group is a dialkyl group, which may be substituted and/or unsaturated, and/or wherein the thio group is a dithio group.

10. A process according to claim 9, wherein the organic group is a di-C_{1-6}alkyl group and/or the thio group is a dithio group or a diseleno group.

11. A process according to claim 10, wherein the organic group is a diethyl group.

12. A process according to any one of the preceding claims, wherein the dispersing medium is at a temperature of 250°C or more, preferably about from 300°C to 350°C.

13. A process according to any one of the preceding claims, wherein the dispersing medium passivates the surface of the nanocrystalline material.

14. A process according to any one of the preceding claims, wherein the dispersing medium is TOPO, or a related coordinating medium, including combinations thereof.

15. A process according to any one of the preceding claims, wherein the nanocrystalline material comprises or is selected from any one of cadmium selenide, cadmium sulphide, zinc selenide, zinc sulphide, indium phosphide and gallium arsenide, including ternary and quaternary combinations thereof.

16. A process according to any one of the preceding claims, wherein the nanocrystalline material is cadmium selenide.

17. A process according to any one of the preceding claims, wherein the metal complex is diethyl diselenocarbamato cadmium or dithio diselenocarbamato cadmium, or related mixed alkyl complexes thereof.

18. A nanocrystalline material obtained by the process according to any one of the preceding claims.

19. A device comprising a nanocrystalline material according to claim 18.

20. A device according to claim 19 wherein the device is an optical device.

21. A device according to claim 19 or claim 20 wherein the device is any one of a non-linear optic device, a solar cell or an LED.

22. A device according to any one of claims 19 to 21 wherein the device is an LED.

23. A process substantially as described herein.

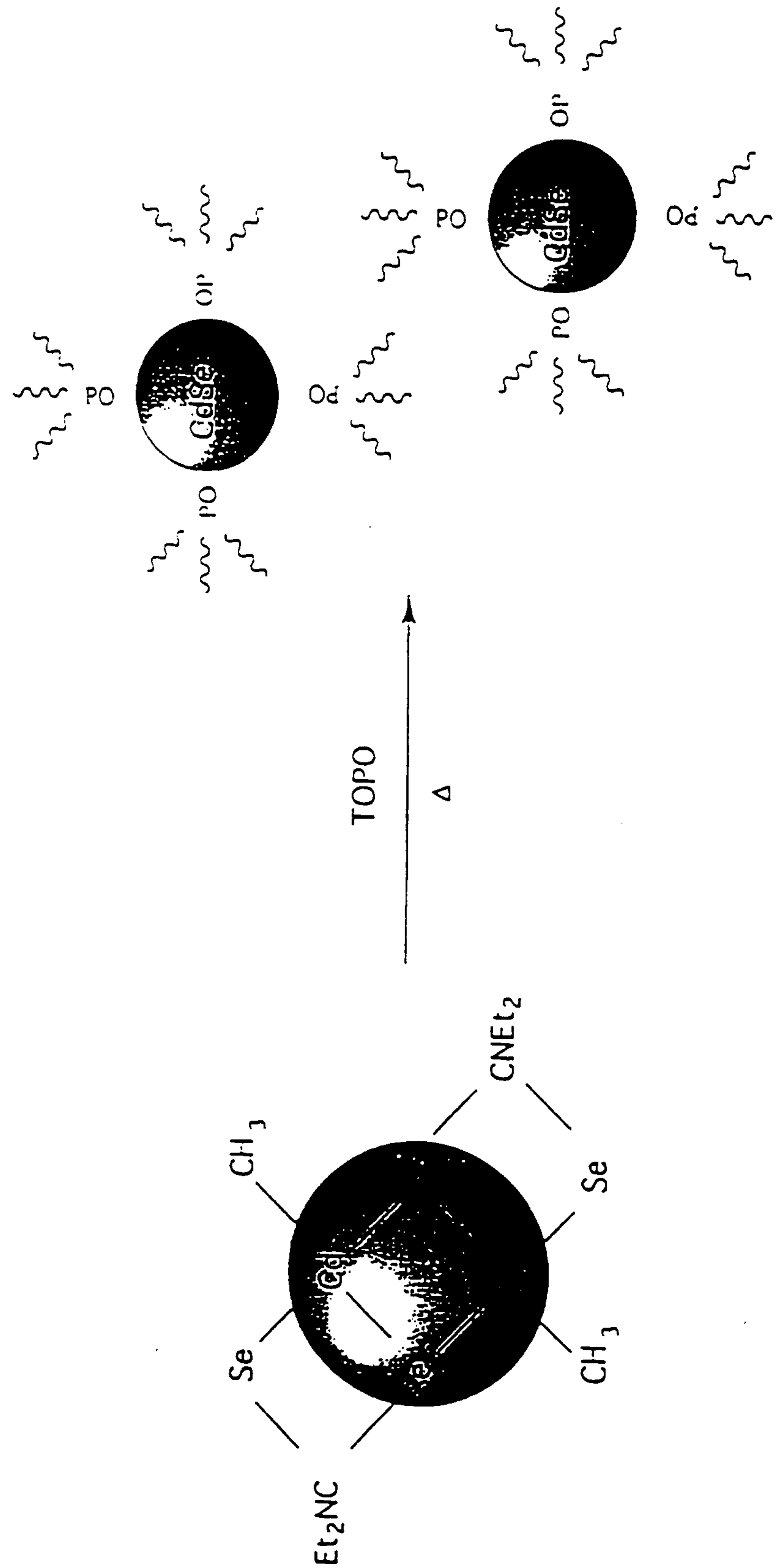
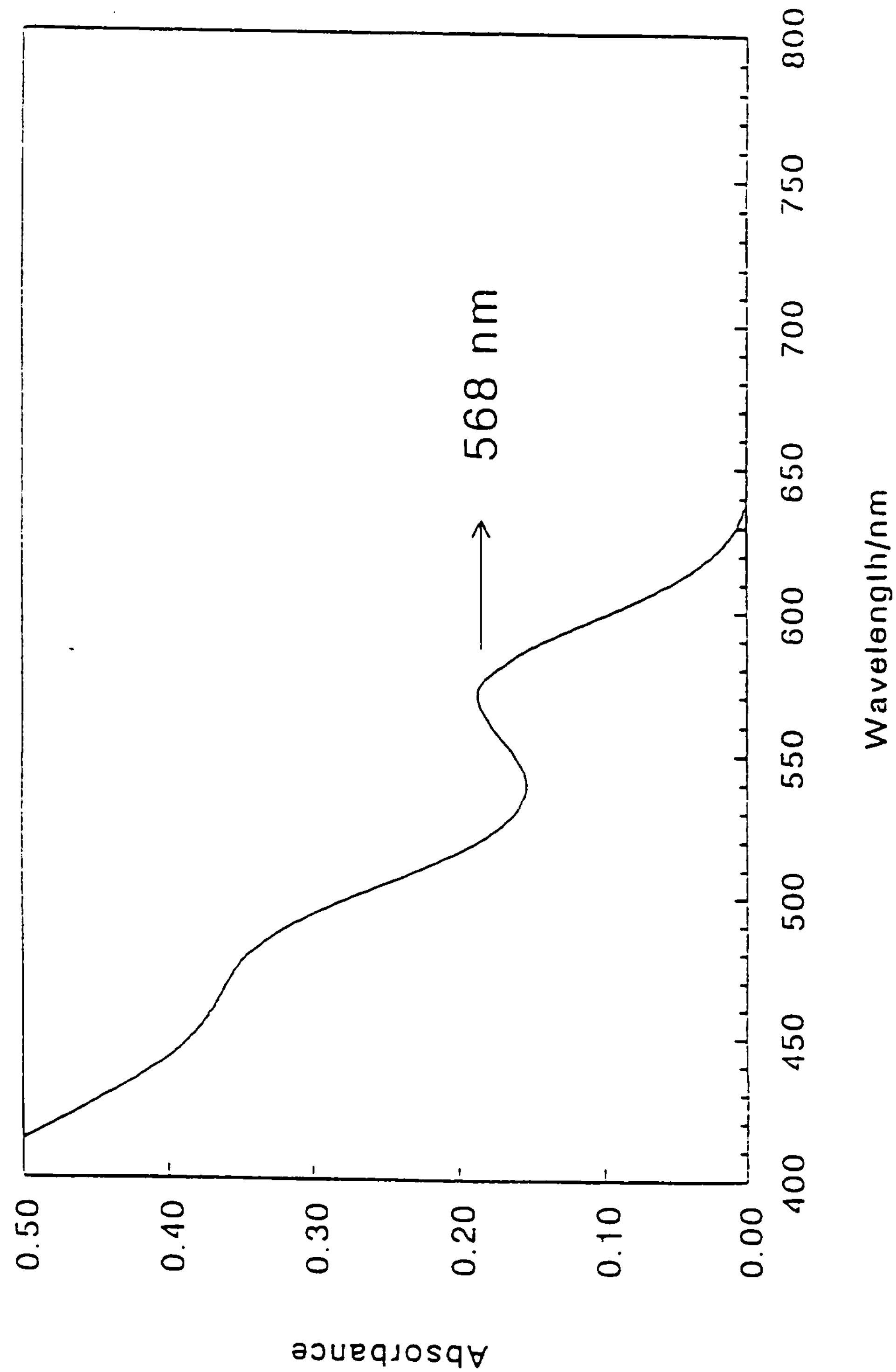


Fig 1

Figure 2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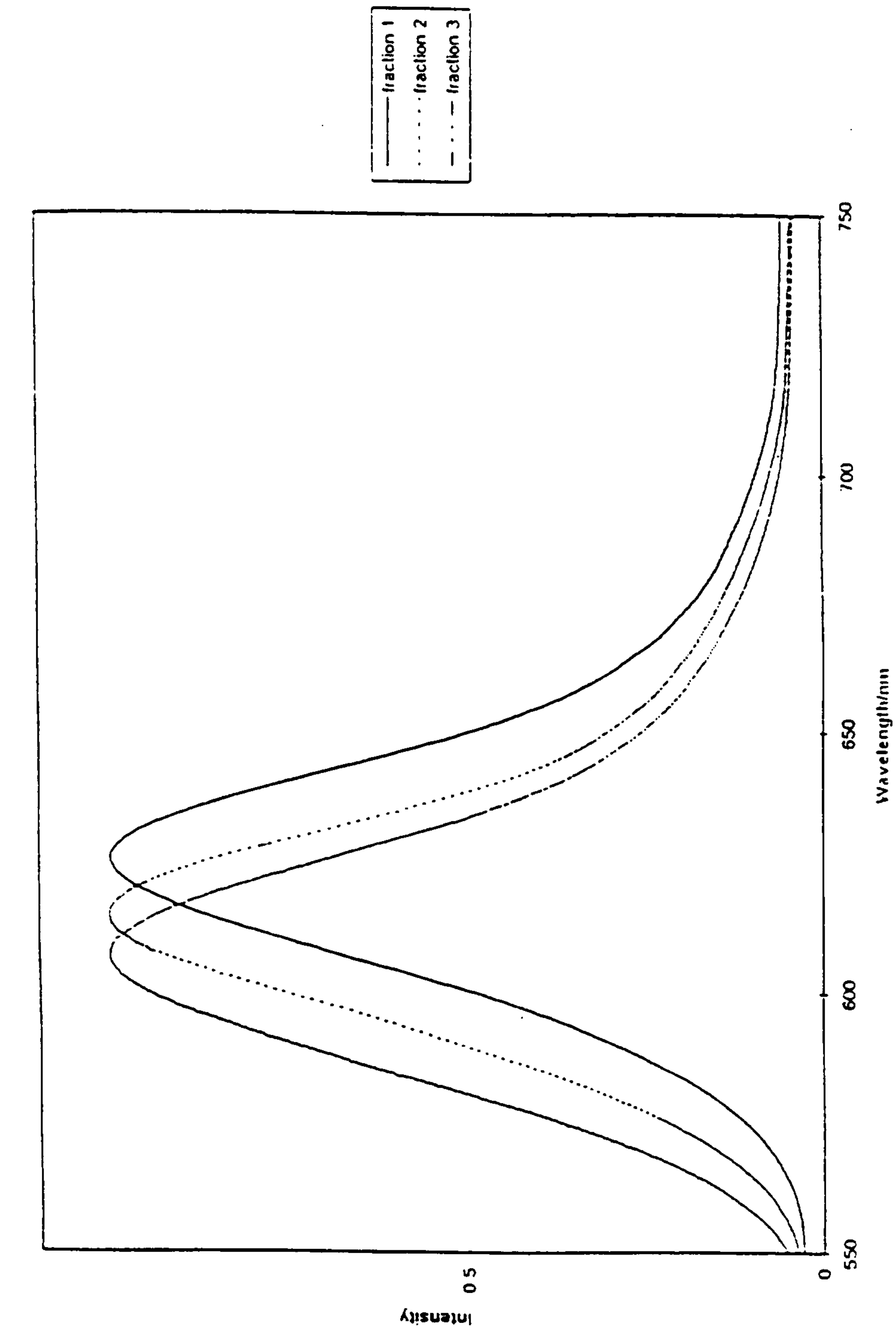
0.40
0.30
0.20
0.10
0.00
400
450
500
550
600
650
700
750
800
Wavelength/nm
Absorbance

Figure 3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fraction 2
fraction 3
Intensity
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0
550
600
650
700
750
Wavelength/nm

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 96/01942

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C01B19/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C01B C01G C30B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 111, 1989, pages 4141-4143, XP000196556 J. G. BRENNAN ET AL: cited in the application see page 4142, line 3 - line 29 ---	
A	JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 112, 1990, pages 1327-1332, XP000196554 A. R. KORTAN ET AL: "Nucleation and growth of CdSe on ZnS quantum crystallite seeds, and vice versa, in inverse micelle media" cited in the application see page 1328 ---	1

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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2

Date of the actual completion of the international search	Date of mailing of the international search report
29 October 1996	19.11.96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Clement, J-P

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Intern   al Application No
PCT/GB 96/01942

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 115, 1993, pages 8706-8715, XP000196555 C. B. MURRAY ET AL: "Synthesis and characterization of nearly monodisperse CdE (E = S, Se, Te) semiconductor nanocrystallites" cited in the application see page 8706 - page 8707 ---	
A	CHEMISTRY OF MATERIALS, vol. 2, no. 2, 1 March 1990, pages 141-149, XP000150666 JOHNSON C E ET AL: "PREPARATION, PURIFICATION, AND DENSIFICATION OF ZINC SULFIDE POWDER FROM ORGANOMETALLICS" see page 142 ---	1
A	WO,A,95 20693 (UNIV DUKE) 3 August 1995 see claim 1 ---	1
A	US,H,H459 (ANN E. STANLEY) 5 April 1988 see claim 1 -----	1

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Inten ial Application No
PCT/GB 96/01942

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9520693	03-08-95	US-A- 5474591	12-12-95
		AU-A- 1729995	15-08-95
US-H-H459	05-04-88	NONE	